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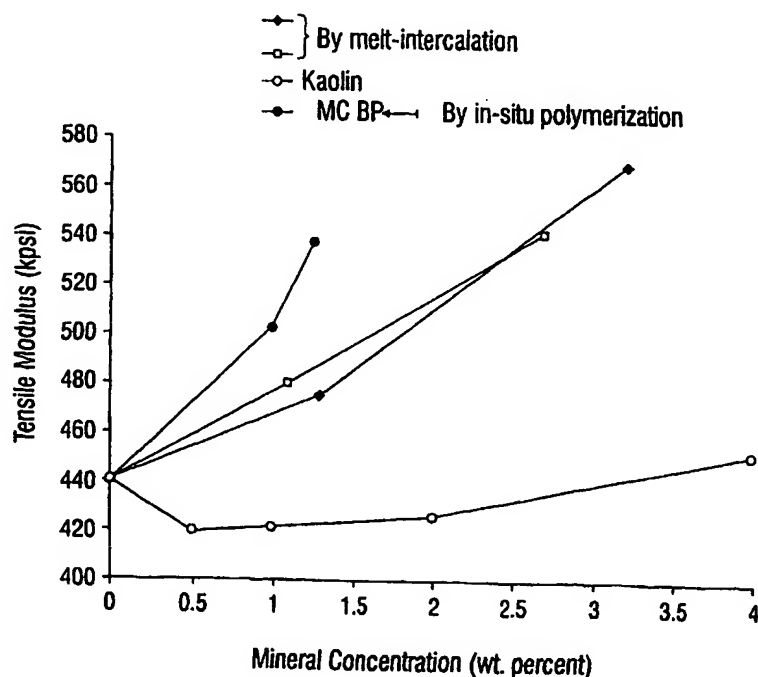
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(54) Title: METHODS FOR THE PREPARATION OF POLYAMIDE NANOCOMPOSITE COMPOSITIONS BY IN SITU POLYMERIZATION



(57) Abstract: In situ polymerization of polyamide monomers and silicate materials produces polyamide nanocomposite materials with desirable physical properties. The nanocomposite materials produced include homopolymers and copolymers. The properties of the nanocomposite materials may be varied by the choice of monomers, type of silicate, and polymerization conditions.

-1-

**METHODS FOR THE PREPARATION OF POLYAMIDE NANOCOMPOSITE
COMPOSITIONS BY IN SITU POLYMERIZATION**

5 Field of the Invention

This invention relates to a nanocomposite material comprising a polyamide matrix having dispersed therein a treated silicate. More particularly, this invention relates to a nanocomposite material having dispersed therein a silicate material treated with at least one ammonium ion.

10 Background of the Invention

International Application WO 93/04118 discloses a process of preparing a polymer nanocomposite having platelet particles dispersed therein. The process involves melt-processing the polymer with a swellable and polymer-compatible intercalated layered material and subjecting it to a shear rate sufficient to dissociate the layers. The layered material is compatibilized with one or more "effective swelling/compatibilizing agents" having a silane function or an onium cation function.

20 International Application WO 93/04117 discloses a process of preparing a polymer nanocomposite having platelet particles dispersed therein, where the polymer and the swellable and polymer-compatible intercalated layered material are melt-processed. The layered material is compatibilized with one or more "effective swelling/compatibilizing agents" selected from primary ammonium, secondary ammonium and quaternary phosphonium ions. The selected swelling/compatibilizing agents "...render their surfaces more organophilic than those compatibilized by tertiary and quaternary ammonium ion complexes...", facilitate exfoliation, resulting in less shear in mixing and less decomposition of the polymer, and heat stabilize the composite more than other cations (such as quaternary ammonium cation) swelling/compatibilizing agents.

-2-

International Patent Application WO 94/22430 discloses a nanocomposite composition having a polymer matrix comprising at least one gamma phase polyamide, and dispersed in the polyamide is a matrix of a nanometer-scale particulate material. The addition of the particulate material to nylon 6 resulted in an improvement of flexural modulus and flexural strength (from 7 to 35%), when compared to unfilled nylon 6. The addition of the particulate material to nylon 6,6 resulted in very little improvement (1 to 3%) of flexural modulus and flexural strength when compared to unfilled nylon 6,6.

International Patent Application WO 93/10098 discloses a polymer composite made by melt-processing a polymer with swellable and polymer-compatible intercalated layered material comprising layers having reactive organo-silane species covalently bonded to their surfaces.

International Patent Application WO 95/14733 discloses a method of producing a polymer composite that does not demonstrate melting or glass transition by melt-processing a polymer with a layered gallery-containing crystalline silicate. The examples include intercalated sodium silicate and a crystalline poly(ethylene oxide), montmorillonite intercalated with a quaternary ammonium and polystyrene, and montmorillonite intercalated with a quaternary ammonium and nylon 6.

None of the above references, alone or in combination, disclose the present invention, as claimed.

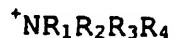
Summary of the Invention

This invention relates to a polymer nanocomposite composition suitable for automotive, electronic, film and fiber applications, where a combination of tensile strength, tensile modulus and flexural modulus are required. Additionally, the claimed polymer nanocomposite composition also has a desirable surface appearance, toughness, ductility and dimensional

-3-

stability. The composition processes well and tolerates a wide range of molding conditions.

Such polymer nanocomposite composition comprises a polyamide and a treated silicate, wherein the treated silicate includes a silicate material treated with at least one ammonium ion of the formula:



wherein:

R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether. Examples include saturated or unsaturated alkyls, including alkylenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxys, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such as alkylaryls, alkyoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like. Optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen. The milligrams of treatment per 100 grams of silicate (MER) of the treated silicate, described in more detail below, is from about 10 milliequivalents/100 g below the cation exchange capacity of the untreated silicate to about 30 milliequivalents/100 g above the cation exchange capacity of the untreated silicate. The composite polymer matrix material demonstrates, when tested, an improvement in tensile modulus and flexural modulus, without a substantial decrease in tensile strength, when compared to that of the polymer without the treated silicate. As utilized herein, "substantial decrease" means a decrease exceeding the statistically determined deviations.

The present invention further relates to a process to prepare the above polymer nanocomposite composition comprising forming a flowable mixture of a polyamide and a treated silicate

~~4~~

material and dissociating (as that term is described in more detail below) at least about 50% but not all of the treated silicate. The treated silicate is a silicate material treated with at least one ammonium ion of the formula:



wherein:

R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether. Examples include saturated or
10 unsaturated alkyls, including alkenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxy, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such
15 as alkylaryls, alkoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like. Optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen. The milligrams of treatment per 100 grams of silicate (MER) of the treated silicate, described in more detail below, is from about 10 milliequivalents/100 g below the cation exchange
20 capacity of the untreated silicate to about 30 milliequivalents/100 g above the cation exchange capacity of the untreated silicate. The composite polymer matrix material demonstrates, when tested, an improvement in tensile modulus and flexural modulus, without a significant decrease in tensile
25 strength, when compared to that of the polymer without the treated silicate.

Description of the Preferred Embodiments
of the Invention

Polyamides of the present invention are synthetic linear
30 polycarbonamides characterized by the presence of recurring carbonamide groups as an integral part of the polymer chain which are separated from one another by at least two carbon atoms. Polyamides of this type include polymers, generally known in the

-5-

art as nylons, which can be obtained from diamines and dibasic acids having the recurring unit represented by the general formula:



- 5 in which R_5 is an alkylene group of at least 2 carbon atoms, preferably from about 2 to about 11 or arylene having at least about 6 carbon atoms, preferably about 6 to about 17 carbon atoms; and R_6 is selected from R_5 and aryl groups. Also, included are copolyamides, terpolyamides and the like obtained by
10 known methods, for example, by condensation of hexamethylene diamine and a mixture of dibasic acids consisting of terephthalic acid and adipic acid. Polyamides of the above description are well-known in the art and include, for example, poly(hexamethylene adipamide) (nylon 6,6), poly(hexamethylene sebacamide) (nylon 6,10), poly(hexamethylene isophthalamide),
15 poly(hexamethylene terephthalamide), poly(heptamethylene pimelamide) (nylon 7,7), poly(octamethylene suberamide) (nylon 8,8), poly(nonamethylene azelamide) (nylon 9,9), poly(decamethylene sebacamide) (nylon 10,9), poly(decamethylene sebacamide) (nylon 10,10), poly[bis(4-amino cyclohexyl)methane-1,10-decanecarboxamide)], poly(m-xylene adipamide), poly(p-xylene sebacamide), poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(piperazine sebacamide), poly(p-phenylene terephthalamide), poly(metaphenylene isophthalamide), and copolymers and
20 terpolymers of the above polymers. Additional polyamides include nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons and their copolymers.

Other useful polyamides are those formed by polymerization of amino acids and derivatives thereof, as for example, lactams.

- 30 Illustrative of these useful polyamides are poly(caprolactam) (nylon 6), poly(4-aminobutyric acid) (nylon 4), poly(7-aminoheptanoic acid) (nylon 7), poly(8-aminooctanoic acid) (nylon 8), poly(9-aminononanoic acid) (nylon 9), poly(10-aminodecanoic

-6-

acid) (nylon 10), poly(11-aminoundecanoic acid) (nylon 11), poly(12-aminododecanoic acid) (nylon 12) and the like.

5 The preferred polyamide is Vydyne® nylon, which is poly(hexamethylene adipamide) (nylon 6,6), which gives a composite with the desired combination of tensile strength, tensile modulus and flexural modulus for the applications contemplated herein (Vydyne® is a registered trademark of Solutia, Inc.).

10 The preferred molecular weight of the polyamide is in the range of 30,000 to 80,000 D (weight average) with a more preferred molecular weight of at least 40,000 D (weight average).

Increasing the weight average molecular weight of the polyamide from about 35,000 to 55,000 D results in an unexpected increase in toughness as indicated by the notched izod impact test.

15 Whereas an increase in the weight average molecular weight of from about 35,000 to 55,000 D in the polyamide neat results in a small increase in toughness, the same increase in molecular weight in the nanocomposite results about twice the increase in toughness. Therefore, the increase in toughness is enhanced in

20 the nanocomposite when compared to that of the polyamide neat.

In a preferred embodiment, the polyamide has an amine end group/acid end group ratio greater than one (1). More preferably, the concentration of amine end groups is at least 10 mole % greater than the concentration of the carboxylic acid end

25 groups. In an even more preferred embodiment, the polyamide has a concentration of amine end groups at least 20 mole % greater than the concentration of the carboxylic acid end groups, and in a most preferred embodiment, the polyamide has a concentration of amine end groups at least 30 mole % greater than the

30 concentration of the carboxylic acid end groups. In another embodiment, the concentration of amine end groups is essentially equal to the concentration of carboxylic acid end groups.

-7-

Among the preferred embodiments is nylon 6, nylon 6,6, blends thereof and copolymers thereof. The range of ratios of the nylon 6/nylon 6,6 in the blends is from about 1/100 to 100/1.

Preferably, the range is from about 1/10 to 10/1. The range of ratios of the nylon 6/nylon 6,6 in the copolymers is about 1/100 to 100/1. Preferably, the range is from about 1/10 to 10/1.

Optionally, the nanocomposite composition comprises at least one additional polymer. Examples of suitable polymers include polyethyleneoxide, polycarbonate, polyethylene, polypropylene, poly(styrene-acrylonitrile), poly(acrylonitrile-butadiene-styrene), poly(ethylene terephthalate), poly(butylene terephthalate), poly(trimethylene terephthalate), poly(ethylene naphthalate), poly(ethylene terephthalate-co-cyclohexane dimethanol terephthalate), polysulphone, poly(phenylene oxide) or poly(phenylene ether), poly(hydroxybenzoic acid-co-ethylene terephthalate), poly(hydroxybenzoic acid-co-hydroxynaphthenic acid), poly(esteramide), poly(etherimide), poly(phenylene sulfide), poly(phenylene terephthalamide).

The mixture may include various optional components which are additives commonly employed with polymers. Such optional components include surfactants, nucleating agents, coupling agents, fillers, impact modifiers, chain extenders, plasticizers, compatibilizers, colorants, mold release lubricants, antistatic agents, pigments, fire retardants, and the like.

Suitable examples of fillers include carbon fiber, glass fiber, kaolin clay, wollastonite and talc. Suitable examples of compatibilizers include acid-modified hydrocarbon polymer, such as maleic anhydride-grafted propylethylene, maleic anhydride-grafted polypropylene, maleic anhydride-grafted ethylenebutylene-styrene block copolymer. Suitable examples of mold release lubricant includes alkyl amine, stearamide, and di-or tri-aluminum stearate.

-8-

Suitable examples of impact modifiers include ethylene-propylene rubber, ethylene-propylene diene rubber, methacrylate-butadiene-styrene (with core-shell morphology), poly(butylacrylate) with or without carboxyl modification, 5 poly(ethylene acrylate), poly(ethylene methylacrylate), poly(ethylene acrylic acid), poly(ethylene acrylate) ionomers, poly(ethylene methacrylate acrylic acid) terpolymer, poly(styrene-butadiene)block copolymers, poly(styrene-butadiene-styrene)block terpolymers, poly(styrene-ethylene/butylene-10 styrene) block terpolymers and poly(styrene-ethylene/butylene-styrene carboxylate) block terpolymers.

Silane coupling agents are well-known in the art and are useful in the present invention. Examples of suitable coupling agents include octadecyltrimethoxysilane, gamma-15 aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, gamma-aminopropylphenyldimethoxysilane, gamma-glycidopropyl tripropoxysilane, 3,3-epoxycyclohexylethyl trimethoxysilane, gamma-propionamido trithoxysilane, N-trimethoxysilylpropyl-N(beta-aminoethyl) amine, trimethoxysilylundecylamine, 20 trimethoxysilyl-2-chloromethylphenylethane, trimethoxysilylethylphenylsulfonylazide, N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride, N-(trimethoxysilylpropyl)-N-methyl-N,N-diallylammonium chloride, trimethoxysilylpropylcinnamate, 3-mercaptopropyl 25 trimethoxysilane, 3-isocyanatopropyltriethoxysilane, and the like. The preferred silane is gamma-aminopropyltriethoxysilane.

The silane coupling agent is optionally added to the polymer composite in the range of about 0.5 to 5 weight % of the layered silicate. The preferred concentration range of silane coupling 30 agent is about 1 to 3 weight % of the layered silicate in the composite.

In one embodiment, the nanocomposite composition further comprises a composition wherein an acid end group of the

-9-

polyamide is bonded to a surface of the treated layered silicate by a silane coupling agent.

The silicate materials of the present invention are selected from the group consisting of layered silicates and fibrous, chain-like silicates, and include phyllosilicates. Examples of fibrous, chain-like silicates include chain-like minerals, for example sepiolite and attapulgite, with sepiolite being preferred. Such silicates are described, for example, in Japanese Patent Application Kokoku 6-84435 published October 26, 1994. Examples of layered silicates include layered smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, Laponite® synthetic hectorite, natural hectorite, saponite, sauconite, magadiite, and kenyaite; vermiculite; and the like. Other useful materials include layered illite minerals such as ledikite and admixtures of illites with one or more of the clay minerals named above. The preferred layered silicates are the smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, Laponite® synthetic hectorite, natural hectorite, saponite, sauconite, magadiite, and kenyaite.

The layered silicate materials suitable for use in the present invention are well-known in the art, and are sometimes referred to as "swellable layered material". A further description of the claimed layered silicates and the platelets formed when melt processed with the polyamide is found in International Patent Application WO 93/04117, which is hereby incorporated by reference. The layered silicate materials typically have planar layers arrayed in a coherent, coplanar structure, where the bonding within the layers is stronger than the bonding between the layers such that the materials exhibit increased interlayer spacing when treated.

The layered silicate materials require treatment as described in more detail below with the subject ammonium ion to

-10-

provide the interlayer swelling and/or spacing required for the performance of the treated silicate of the present invention. As used herein the "inter layer spacing" refers to the distance between the faces of the layers as they are assembled in the treated material before any delamination (or exfoliation) takes place. The preferred clay materials generally include interlayer or exchangeable cations such as Li^+ , Na^+ , Ca^{+2} , K^+ , Mg^{+2} and the like. In this state, these materials have interlayer spacings usually equal to or less than about 4 Å and only delaminate to a low extent in host polymer melts regardless of mixing. In the claimed embodiments, the cationic treatment is an ammonium species which is capable of exchanging with the interlayer cations such as Li^+ , Na^+ , Ca^{+2} , K^+ , Mg^{+2} and the like in order to improve delamination of the layered silicate.

The treated silicate of the present invention is a silicate material as described above which is treated with at least one ammonium ion of the formula



wherein:

R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether. Examples include saturated or unsaturated alkyls, including alkenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxys, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such as alkylaryls, alkoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like. Optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen. A mixture of two or more ammonium ions is contemplated by the present invention.

In a preferred embodiment of the present invention, R_1 is selected from the group consisting of hydrogenated tallow,

-11-

unsaturated tallow or a hydrocarbon having at least 6 carbons, and R₂, R₃ and R₄ independently have from one to eighteen carbons.

Tallow is composed predominantly of octadecyl chains with small amounts of lower homologues, with an average of from 1 to 2 degrees of unsaturation. The approximate composition is 70% C₁₈, 25% C₁₆, 4% C₁₄ and 1% C₁₂. In another preferred embodiment of the present invention, R₁ and R₂ are independently selected from the group consisting of hydrogenated tallow, unsaturated tallow or a hydrocarbon having at least 6 carbons and R₃ and R₄ independently have from one to twelve carbons.

Examples of suitable R₁, R₂, R₃ and R₄ groups are alkyl such as methyl, ethyl, octyl, nonyl, tert-butyl, ethylhexyl, neopentyl, isopropyl, sec-butyl, dodecyl and the like; alkenyl such as 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl and the like; cycloalkyl such as cyclohexyl, cyclopentyl, cyclooctyl, cycloheptyl and the like; alkoxy such as ethoxy; hydroxyalkyl; alkoxyalkyl such as methoxymethyl, ethoxymethyl, butoxymethyl, propoxyethyl, pentoxybutyl and the like; aryloxyalkyl and aryloxyaryl such as phenoxyphenyl, phenoxymethyl, phenoxydecyl, phenoxyoctyl and the like; arylalkyl such as benzyl, phenylethyl, 8-phenyloctyl, 10-phenyldecyl and the like, alkylaryl such as 3-decylphenyl, 4-octylphenyl, nonylphenyl and the like.

The preferred ammoniums used in treating the silicate materials include oniums such as dimethyldi(hydrogenated tallow) ammonium, dimethylbenzyl hydrogenated tallow ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium, trimethyl hydrogenated tallow ammonium, methylbenzyl di(hydrogenated tallow) ammonium, N,N-2-cyclobutoxy di(hydrogenated tallow) ammonium, trimethyl tallow ammonium, methyldihydroxyethyl tallow ammonium, octadecylmethyldihydroxyethyl ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium and mixtures thereof. Particularly preferred ammoniums include quaternary ammoniums, for example,

-12-

dimethyldi(hydrogenated tallow) ammonium, dimethylbenzyl
hydrogenated tallow ammonium, methyldihydroxyethyl tallow
ammonium, octadecylmethyldihydroxyethyl ammonium,
dimethyl(ethylhexyl) hydrogenated tallow ammonium and mixtures
5 thereof.

The treatment with the ammonium ion(s), also called
"cationic treatments", may include introduction of the ions into
the silicate material by ion exchange. In the embodiment where
the silicate material is a layered silicate, the cationic
10 treatments may be introduced into the spaces between every layer,
nearly every layer, or a large fraction of the layers of the
layered material such that the resulting platelet layers comprise
less than about 20 particles in thickness. The platelet layers
are preferably less than about 8 particles in thickness, more
15 preferably less than about 5 particles in thickness, and most
preferably, about 1 or 2 particles in thickness.

The treated silicate has a MER of from about 10
milliequivalents/100 g below the cation exchange capacity of the
untreated silicate to about 30 milliequivalents/100 g above the
20 cation exchange capacity of the untreated silicate. The MER is
the milliequivalents of treatment per 100 g of silicate. Each
untreated silicate has a cation exchange capacity, which is the
milliequivalents of cations available for exchange per 100 g of
silicate. For example, the cation exchange capacity of the
25 layered silicate montmorillonite can be about 95, and the
exchange capacity of sepiolite is in the range of about 25 to 40.

When the MER of the treated silicate substantially exceeds the
cation exchange capacity, there is an excess of cationic
treatment which may be available to react with the polyamide.
30 This excess may cause degradation of the properties of the
polyamide.

The higher the MER, the lower the concentration of
silicate in the treated silicate. Therefore, a first

-13-

nanocomposite sample may have a higher concentration of treated silicate but a lower concentration of silicate, than a second nanocomposite sample, because the first sample has a higher MER than the second sample.

5 If the MER value of the treated silicate is substantially less than its exchange capacity, for example about 85 MER for the preferred montmorillonite, there is too little of the cationic treatment to have a beneficial effect. If the MER exceeds about 125, the excess ammonium may be detrimental to the properties of
10 the nylon. Preferably, when the untreated montmorillonite has an exchange capacity of 95, the treated layered silicate has a cation exchange capacity of from about 85 to about 125.

 The amount of treated silicate included in the composition is in the range of about 0.1 to 12 weight % of the composite.
15 The concentration is adjusted to provide a composite polymer matrix material which demonstrates, when tested, an increase in tensile modulus and flexural modulus, without a decrease in tensile strength. Preferably, the increase in tensile modulus and flexural modulus is at least about 10%. More preferably, the
20 increase in tensile modulus and flexural modulus is at least about 20%. Too little treated silicate fails to provide the desired increase in tensile modulus and flexural modulus. Too much treated silicate provides a polyamide composite with a decreased tensile strength. Further, it may be desirable to have
25 the crystalline regions of the polyamide in the nanocomposite composition be less than 1.0 μ m.

 The particle size of the treated silicate is such that optimal contact between the polymer and the treated silicate is facilitated. The range of particle size can vary from about 10
30 microns to about 100 microns. Preferably, the particle size is in the range of from about 20 to 80 microns. Most preferably, the particle size is below about 30 microns, such as those that

-14-

pass through 450 mesh screens, in that the resulting polymer nanocomposite has improved performance properties.

Optionally, the silicate can be treated with a mixture of one or more quaternary ammonium ions with one or more ammonium ions of the formula



wherein at least one of R_a , R_b and R_c is hydrogen (H) and R_d is selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched

hydrocarbon. Examples include saturated or unsaturated alkyls, including alkenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxys, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such as alkylaryls, alkoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like.

As the definition of the R_d group for the ammonium ion above is generally the same as the definition for the R_4 group in the ammonium ion, which in this embodiment is a quaternary ammonium, the Examples set forth above for the R_4 group are also exemplary of the R_d group. Optionally, the R_d group further contains a carboxylic acid moiety such that the ammonium ion



is an amino acid, for example 12-aminolauric acid ammonium. In this embodiment, it is particularly preferred that the amine end groups/acid end groups ratio of the polyamide is greater than one (1).

A preferred mixture includes at least one of dimethyldi(hydrogenated tallow) ammonium, methyl dihydroxyethyl tallow ammonium and/or dimethyl(ethylhexyl) hydrogenated tallow ammonium, either alone or in combination with 12-aminolauric acid ammonium.

Optionally, the treated silicate can be further treated with azine cationic dyes, such as nigrosines or anthracenes.

• -15-

Said cationic dyes would impart color-fastness and uniformity of color in addition to increasing the intercalation of the polymer molecules.

It is further desirable to have a polymer composite that provides both the desired strength and flexibility, and yet is lightweight. This is accomplished by minimizing the concentration of treated silicate in the nanocomposite. The preferred nanocomposite contains a concentration of treated silicate of from about 0.1 to about 12.0 weight % of the composite. The most preferred nanocomposite contains a concentration of treated silicate of from about 0.5 to about 6.0 weight % of the composite.

In a first embodiment of the present invention, the nanocomposite composition is prepared using a two step process. One step includes forming a flowable mixture of the polyamide as a polymer melt and the treated silicate material. The other step includes dissociating at least 50% but not all of the treated silicate material. The term "dissociating", as utilized herein, means delaminating or separating treated silicate material into submicron-scale structures comprising individual or small multiple units. For the embodiment wherein layered silicates are utilized this dissociating step includes delaminating the treated silicate material into submicron scale platelets comprising individual or small multiple layers. For the embodiment wherein fibrous; chain-like silicates are utilized, this dissociating step includes separating the treated silicate material into sub-micron scale fibrous structures comprising individual or small multiple units.

As referred to in the mixture forming step, a flowable mixture is a mixture which is capable of dispersing dissociated treated silicate material at the submicron scale. A polymer melt is a melt processable polymer or mixture of polymers which has been heated to a temperature sufficiently high to produce a

.. -16-

viscosity low enough for submicron scale mixing to occur. The process temperature should be at least as high as the melting point of the polyamide employed and below the degradation temperature of the polyamide and of the organic treatment of the silicate. The actual extruder temperature may be below the melting point of the polyamide employed, because heat is generated by the flow. The process temperature is high enough that the polymer will remain in the polymer melt during the conduct of the process. In the case of a crystalline polyamide, that temperature is above the polymer's melting temperature. For example, a typical nylon 6, having a melting point of about 225°C, can be melted in an extruder at any temperature equal to or greater than about 225°C, as for example between about 225°C and about 260°C. For nylon 6,6 a temperature of preferably from about 260°C to about 320°C is normally employed.

Conventional methods can be employed to form the flowable mixture. For example, the flowable mixture can be prepared through use of conventional polymer and additive blending means, in which the polymer is heated to a temperature sufficient to form a polymer melt and combined with the desired amount of the treated silicate material in a granulated or powdered form in a suitable mixer, as for example an extruder, a Banbury® type mixer, a Brabender® type mixer, Farrel® continuous mixers, and the like.

In one embodiment, the flowable mixture may be formed by mixing the polyamide with a previously formed treated silicate-containing concentrate. The concentrate includes the treated silicate and a polymer carrier. The concentration of the treated silicate material in the concentrate is selected to provide the desired treated silicate concentration for the final nanocomposite composition. Examples of suitable polymers for the carrier polymer of the concentrate include polyamide, ethylene propylene rubber, ethylene propylene diene rubber, ethylene-

. -17-

ethylacrylate, ethylene-ethylmethacrylate or ethylene methacrylate. Examples include Iotek® ionomer and Escor® ATX acid terpolymer, both available from Exxon. The polyamide polymers suitable for the carrier polymer include nylons such as
5 nylon 6, nylon 6,6, nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons and their copolymers. The polymer of the carrier may be the same as or different from the polyamide of the flowable mixture. For
10 example, both polymers may be a polyamide, particularly nylon 6,6, but may have the same or different molecular weight. The preferred weight average molecular weight of the carrier polymer of the concentrate is in the range of about 5,000 D to about 60,000 D. The most preferred range of the weight average
15 molecular weight for the carrier polymer is in the range of about 10,000 to about 40,000 D. In this embodiment, the dissociation step of the present process, as described below, may occur at least in part via the forming of the concentrate such that the dissociation step may precede the step of forming the flowable mixture. It is therefore understood that the process steps
20 (e.g., forming and dissociating) may occur sequentially without regard to order, simultaneously or a combination thereof. In the second step, the flowable mixture is sufficiently mixed to form the dispersed nanocomposite structure of dissociated silicate in the polymer melt, and it is thereafter cooled. The
25 silicate can be dissociated by being subjected to a shear having an effective shear rate. As used herein, an effective shear rate is a shear rate which is effective to aid in dissociation of the silicate and provide a composition comprising a polyamide matrix having silicate substantially homogeneously dispersed therein
30 without substantially breaking the individual units (e.g., platelets or fibrous chains).

Any method which can be used to apply a shear to a flowable mixture or any polymer melt can be used. The shearing

" -18-

action can be provided by any appropriate method, such as by mechanical means, by thermal shock, by pressure alteration, or by ultrasonics. Preferably, the flowable polymer mixture is sheared by mechanical methods in which portions of the melt are caused to flow past other portions of the mixture by use of mechanical means such as stirrers, Banbury® type mixers, Brabender® type mixers, Farrel® continuous mixers, and extruders. Most preferably, the mixture is subjected to multiple shearings. In addition to the increased shear provided by multiple shearing, increased residence time is also provided, which results in improved performance properties. Another procedure employs thermal shock in which shearing is achieved by alternatively raising or lowering the temperature of the mixture causing thermal expansions and resulting in internal stresses which cause the shear. In still other procedures, shear is achieved by sudden pressure changes in pressure alteration methods; by ultrasonic techniques in which cavitation or resonant vibrations which cause portions of the mixture to vibrate or to be excited at different phases and thus subjected to shear. These methods of shearing flowable polymer mixtures and polymer melts are merely representative of useful methods, and any method known in the art for shearing flowable polymer mixtures and polymer melts may be used.

Shearing can be achieved by introducing the polymer pellets at one end of the extruder (single or twin screw) and receiving the sheared polymer at the other end of the extruder. A preferred twin screw extruder is a co-rotating fully intermeshing type, such as the ZSK series manufactured by Werner and Pfleiderer Company. The layered silicate can be fed into the twin screw extruder at the feed throat or at the downstream vent.

The preferred method is to feed the layered silicate at the downstream vent, which produces a composite polymer with improved performance properties.

-19-

Optionally, an additional processing step can be added, such as solid state polymerization, wherein the compounded pellets are held for several hours at a high temperature below the melting point of the polymer. For example, typical solid state polymerization conditions are heating the solid polymer in the range of about 200 to 240°C for a period of from about two (2) to five (5) hours. Said additional processing step results in an increase in molecular weight and an improvement in toughness, ductility and tensile strength of the nanocomposite.

Another optional processing step can be a heat treatment step, where the composition is heated to improve intercalation of the nylon molecules into the silicate structure. Said heat treatment step is performed by heating the composition at a temperature in the range of about 200 to 240°C for a period of about two (2) to five (5) hours.

Another preferred continuous compounder is the Farrel Continuous Mixer (FCM). For composites using Vydyne® 21 nylon, the preferred temperature of the melt is in the range from about 275 to 315°C, with the most preferred range being from about 275 to 295°C.

The polymer melt containing nano-dispersed dissociated silicate material may also be formed by reactive extrusion in which the silicate material is initially dispersed as aggregates or at the nanoscale in a liquid or solid monomer and this monomer is subsequently polymerized in an extruder or the like. Alternatively, the polymer may be granulated and dry mixed with the treated silicate material, and thereafter, the composition may be heated in a mixer until the polymer is melted forming the flowable mixture.

The process to form the nanocomposite is preferably carried out in the absence of air, as for example in the presence of an inert gas, such as argon, neon or nitrogen. The process

-20-

can be carried out in a batchwise or discontinuous fashion, as for example, carrying out the process in a sealed container. Alternatively, the process can be carried out in a continuous fashion in a single processing zone, as for example, by use of an extruder, from which air is largely excluded, or in a plurality of such reaction zones in series or in parallel.

In another embodiment of the present invention, the process to prepare a polymer nanocomposite composition comprises forming a first flowable mixture of a polyamide, at least one monomer, and a treated silicate material; dissociating at least 50% but not all of the treated silicate material and polymerizing the monomer. It is to be understood that the polymerization step can occur simultaneously or sequentially with one or more other steps in the process of this embodiment. Preferably, at least one monomer of the third embodiment includes monomers such as ϵ -caprolactam, lauryllactam, and their corresponding lactones.

In yet another embodiment of the present invention, the process to prepare a polymer nanocomposite composition comprises forming a flowable mixture of a polyamide and a treated silicate material; dissociating the at least about 50% but not all of the treated silicate material; and adding an additional amount of said polyamide, most preferably during said dissociating step.

Each of the above embodiments of the process to prepare the polymer nanocomposite composition can be followed by additional steps or treatments, such as solid state polymerization, or additional melt polymerization of the composition by increasing the residence time in the mixer with the removal of water condensation product.

The composition of the present invention can be made into, but is not limited to, the form of a fiber, film or a molded article.

. -21-

Examples

The following examples are presented to further illustrate the invention and do not limit the scope of the claims in any manner.

5 All of the nylons used in the following examples are nylon 6,6. Unless otherwise indicated, the nylon used was nylon h, manufactured by Solutia, Inc, and characterized in the Table of Nylon Types, below. Unless otherwise indicated, all percents are weight percent. The % clay is the total weight of pristine clay
10 in the final composite, be it pristine or pre-treated. Tensile strength and Young's Modulus are measured according to ASTM method D638 and are reported in kpsi and MPa. Flexural modulus is measured according to ASTM method D790 and is reported in kpsi and MPa.

15 The runs numbered with a "-C" are control runs.

-22-

Table 1 of Clay Types

All of the silicates listed below, unless otherwise identified, are montmorillonites produced by Southern Clay Products Inc. with a clay exchange capacity of about 95. The treatments listed below are ammonium treatments. Items A-H are controls while the items I-AA are examples of quaternary ammonium treated silicates of the present invention.

	<u>Item</u>	<u>Ammonium Treatment</u>	<u>MER</u>
10	A	untreated	--
	B	hectorite, untreated	--
	C	dicyclohexyl	100
	D	12-aminolauric acid	90
15	E	dimethyldi(hydrogenated tallow)	140
	F	dimethylbenzyl hydrogenated tallow	140
	G	dimethyldi(hydrogenated tallow)	140
	H	methylbenzyldi(hydrogenated tallow)	130
20	I	trimethyl tallow	125
	J	dimethyldi(hydrogenated tallow)	80
	K	dimethyldi(hydrogenated tallow)	85
	L	trimethyl hydrogenated tallow	125
	M	dimethyl(ethylhexyl)	
25		hydrogenated tallow	90
	N	dimethyl(ethylhexyl) hydrogenated tallow, with wetting agent	90
	O	dimethyl(ethylhexyl) hydrogenated tallow, with wetting agent	90
30	P	diethoxymethyl tallow	90
	Q	dimethyldi(hydrogenated tallow), fine ground clay, with additional processing	95
	R	octadecylmethyldiethoxy	95
35	S	trimethyl C ₂₂	110
	T	dimethyldi(hydrogenated tallow), better dispersing form	95
	U	dimethyldi(hydrogenated tallow), processed	95
40	V	item U, above, with 1% surfactant	95
	W	dimethyldi(hydrogenated tallow)	125
	X	dimethyldi(hydrogenated tallow), fine ground clay	95
	Y	N,N-2-butoxydi(hydrogenated tallow)	90
45	Z	dimethyldi(hydrogenated tallow)	95

-23-

AA dimethylbenzyl hydrogenated tallow 95

-24-

Table 2 of Clay Types

Items GG through NN are examples of montmorillonite, unless otherwise indicated, treated with the blends of more than one quaternary ammonium or of a quaternary ammonium and ammonium of the present invention. Items OO through TT are examples of the tertiary ammonium silicates of the present invention.

<u>Item</u>	<u>Ammonium Treatment</u>	<u>MER</u>
10 GG ¹	80/20 blend of sepiolite and smectite, treated with 75/25 blend of methylbenzyl di(hydrogenated tallow) and dimethyl di(hydrogenated tallow)	45
15 HH	50/50 blend of 2-ethylhexyl, dimethyl hydrogenated tallow and dimethyl di(hydrogenated tallow)	95
II	25/75 blend of 2-ethylhexyl, dimethyl hydrogenated tallow and dimethyl di(hydrogenated tallow)	95
20 JJ	75/25 blend of 2-ethylhexyl, dimethyl hydrogenated tallow and dimethyl di(hydrogenated tallow)	95
KK	10.5/89.5 blend of 12-aminolauric acid and dimethyl di(hydrogenated tallow)	95
25 LL	16/84 blend of 12-aminolauric acid and dimethyl di(hydrogenated tallow),	95
MM	5/95 blend of 12-aminolauric acid and dimethyl di(hydrogenated tallow)	95
30 NN	16/84 blend of 12-aminolauric acid and dimethyl (ethylhexyl) hydrogenated tallow	95
OO	dimethyl cocoa	95
PP	dimethyl hydrogenated tallow	95
QQ	dimethyl tallow	95
35 RR	2-ethylhexyl methyl hydrogenated tallow	95
SS	dimethyl hydrogenated tallow	95
TT	dihydroxyethyl octadecyl	125

¹ Patent Pending

-25-

Table of Nylon Types

<u>Nylon</u>	<u>Amine Ends</u>	<u>Acid Ends</u>	<u>Amine/Acid</u>	<u>M_w</u> (1000 D)
a	55	60	0.92	35
5 b	35	60	0.58	42
c	40	40	1.00	50
d	15	50	0.30	62
e	80	50	1.60	31
f	125	70	1.79	21
10 g	31	60	0.52	44
h	45	70	0.64	35

The amine ends and the acid ends are the equivalents of unreacted amine and acid functional groups on the nylon. The M_w is the weight average molecular weight as measured in Daltons.

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. -26- .

In Table 1, composites of four (4) different types of treated clay are shown. The control examples using clays not treated with ammoniums of the present invention show a general decrease in tensile strength when compared to the preceding (i.e. comparable) sample containing no clay (i.e., comparing 2-C, 3-C and 4-C to 1-C and comparing 6-C, 7-C and 8-C to 5-C), with the exception of control example 3-C which shows no change in tensile strength when compared to 1-C.

10 Runs 1-C through 4-C were processed with a ZSK twin screw extruder, and runs 5-C through 8-C were processed with a FCM mixer.

-27-

Table 1
Control Runs
(Clays not treated with Quaternary Amines)

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
1-C	--	0	11.6 (80.3)	412 (2860)	425 (2940)	286
2-C	A	3.6	11.2 (77.7)	449 (3110)	463 (3210)	285
3-C	A	6.5	11.6 (80.7)	466 (3230)	463 (3210)	286
4-C	B	7.1	11.3 (78.1)	481 (3330)	482 (3340)	286
5-C	--	0	11.6 (80.7)	445 (3080)	436 (3020)	280
6-C	C	2.9	9.65 (66.9)	494 (3420)	481 (3330)	291
7-C	C	8.8	8.08 (56.0)	576 (3990)	568 (3940)	293
8-C	D	4.8	9.11 (63.1)	580 (4020)	550 (3810)	285

-28-

In Table 2, composites of four different treated quaternary ammonium-treated clays with a MER exceeding 125 are shown. The composites were processed using a ZSK mixer. All of the control examples show a decrease in tensile strength when
5 compared to the preceding (corresponding) sample without clay.

Table 2
Control Runs
(Treated Clays with MER's Exceeding 125)

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
9-C	--	0	11.3 (78.3)	417 (2980)	432 (2990)	286
10-C	G	13.3	9.78 (67.8)	610 (4230)	613 (4250)	286
11-C	--	0	11.2 (77.4)	423 (2930)	416 (2880)	277
12-C	E	4.2	10.6 (73.4)	520 (3600)	455 (3150)	277
13-C	E	4.4	10.6 (73.2)	500 (3460)	471 (3260)	279
14-C	E	9.6	9.48 (65.7)	553 (3830)	501 (3470)	285
15-C	--	0	11.3 (78.4)	430 (2980)	445 (3080)	286
16-C	H	11.6	7.47 (51.8)	582 (4030)	573 (3970)	291
17-C	H	11.8	7.73 (53.6)	561 (3890)	549 (3760)	285
18-C	H	6.0	10.6 (73.1)	523 (3620)	516 (3580)	288
19-C	H	11.8	5.41 (37.5)	593 (4110)	571 (3960)	295
20-C	H	6.0	10.5 (72.6)	510 (3530)	507 (3510)	283
21-C	H	8.9	10.3 (71.1)	555 (3850)	541 (3750)	289
22-C	--	0	12.0 (82.9)	424 (2940)	432 (3850)	285
23-C	F	7.3	11.2	557	555	287

-30-

In Table 3, composites prepared from thirteen (13) different quaternary ammonium-treated clay processed with a FCM compounder are shown. All of the composites except 35, 36 and 47, show an increase in tensile modulus and flexural modulus without a decrease in tensile strength when compared with nylon without the treated clay. However, taking into account the standard deviation of samples 35, 36 and 47, the samples could provide a tensile strength equal to or higher than that of their controls.

Table 3
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flex Modulus (MPa)	Melt Temp. (°C)
24-C	--	0	11.6 (80.7)	445 (3080)	436 (3020)	280
25	P	3.0	12.5 (86.3)	580 (4020)	539 (3740)	292
26	P	5.8	11.6 (80.7)	657 (4550)	633 (4390)	293
27	S	3.3	12.1 (84.0)	524 (3630)	524 (3630)	291
28	T	5.4	12.0 (83.2)	596 (4130)	558 (3870)	288
29-C	--	0	11.4 (78.7)	443 (3070)	425 (2940)	285
30	I	1.8	11.6 (80.4)	509 (3530)	470 (3260)	286
31	R	0.6	12.4 (85.9)	482 (3340)	457 (3170)	286
32	M	0.6	11.5 (79.8)	457 (3170)	438 (3040)	285
33	N	1.6	12.1 (83.9)	504 (3490)	474 (3280)	286
34-C	--	0	11.5 (79.5)	463 (3190)	429 (2960)	286
35	J	1.0	10.3 ¹ 453 (71.5)	448 (3140)	284 (3100)	284
36	J	3.3	11.3 ² 500 (78.5)	496 (3460)	288 (3440)	286
37	L	2.5	12.0 (83.4)	525 (3640)	502 (3480)	284
38	L	3.3	11.8 (81.6)	535 (3710)	516 (3580)	286
¹ ±1.44		² ±0.98				

-32-

Table 3, Continued
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
39	W	1.7	11.8 (81.8)	462 (3200)	474 (3280)	285
40	W	4.7	11.7 (80.9)	523 (3620)	507 (3510)	286
41	K	0.8	11.7 (80.9)	449 (3110)	450 (3120)	285
42	K	2.3	11.8 (81.8)	474 (3280)	476 (3300)	286
43	Y	2.6	11.7 (81.1)	476 (3300)	482 (3340)	285
44	Y	4.7	12.1 (83.9)	546 (3780)	525 (3640)	285
45-C	--	0	11.5 (79.8)	469 (3250)	428 (2970)	281
46	Q	1.4	12.1 (83.6)	513 (3560)	478 (3310)	291
47	Q	5.7	11.4 ¹ (79.3)	614 ¹ (4260)	559 ¹ (3870)	294
1 ± 0.4						

-33-

In Table 4, composites are prepared from eight (8) different quaternary ammonium-treated clay processed with a ZSK twin screw extruder are shown. All of the composites show an increase in tensile modulus and flexural modulus without a decrease in tensile strength when compared to samples without treated clay.

Table 4
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
48-C	--	0	11.5 (79.4)	446 (3090)	431 (2990)	285
49	M	1.7	11.7 (81.1)	480 (3330)	476 (3300)	286
50	M	4.1	12.0 (83.2)	543 (3760)	532 (3690)	287
51	N	2.4	11.6 (80.3)	484 (3350)	502 (3480)	287
52	N	4.1	11.5 (79.7)	508 (3520)	470 (3260)	287
53	O	1.9	11.6 (80.1)	462 (3200)	470 (3260)	287
54	O	4.0	11.5 (79.3)	488 (3380)	494 (3420)	287
55-C	--	0	12.0 (82.9)	424 (2940)	432 (2990)	285
56	U	7.5	12.1 (83.6)	525 (3640)	520 (3600)	286
57	V	7.0	12.1 (84.0)	516 (3580)	521 (3610)	285

Table 4, Continued
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
58-C	--	0	11.5 (80.0)	445 (3080)	431 (2990)	287
59	U	2.1	11.8 (82.1)	475 (3290)	483 (3350)	287
60	U	5.2	11.6 (80.1)	560 (4020)	540 (3740)	287
61	U ¹	5.3	12.1 (83.4)	575 (3970)	555 (3830)	287
62	U ²	5.3	12.3 (84.8)	564 (3890)	539 (3720)	288
63-C	--	0	11.31 (78.4)	430 (3880)	445 (3080)	286
64	X	4.9	11.76 (81.5)	606 (4200)	568 (3940)	288
65	X	6.4	11.27 (78.1)	573 (3970)	604 (4190)	295
66-C	--	0	11.55 (79.7)	423 (2930)	424 (2930)	286
67	Q	3.0	11.63 (80.6)	487 (3380)	456 (3160)	286
68	Q	6.5	11.61 (80.5)	514 (3560)	515 (3570)	288
69	Q	11.1	11.60 (80.4)	659 (4570)	579 (4010)	290
70	Q	11.4	12.47 (86.4)	782 (5420)	622 (4310)	289

¹ Second pass of example 60 through ZSK mixer.

² Third pass of example 60 through ZSK mixer.

-36-

Table 4, Continued
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
71-C	--	0	11.3 (77.9)	459 (3170)	446 (3080)	281
72	AA	3.8	12.5 (86.2)	552 (3810)	487 (3360)	282
73	AA	6.8	12.2 (84.1)	562 (3880)	520 (3590)	282
74	AA	8.9	11.5 (79.3)	612 (4220)	553 (3810)	282

-37-

In Table 5, the following four (4) nylon 6,6 products were used to prepare composites: nylon d, nylon c, nylon b, nylon h, shown in the Table of Nylon Types. The nylons are presented above in order of decreasing average molecular weight. The
5 composites were processed using a ZSK twin screw extruder.

All composites show an increase in tensile modulus and flexural modulus without a decrease in tensile strength when compared to samples without treated clay.

Table 5
Varying Nylon Type

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Nylon Type	Melt Temp. (°C)
75-C	--	0	11.3 (78.4)	427 (2960)	430 (2980)	d	291
76	Q	7.3	12.4 (86.0)	600 (4160)	559 (3870)	d	290
77-C	--	0	11.6 (80.4)	402 (2790)	435 (3010)	c	289
78	Q	7.6	12.6 (87.3)	640 (4440)	577 (4000)	c	289
79-C	--	0	11.6 (80.4)	405 (2810)	434 (3010)	b	288
80	Q	7.3	12.0 (83.2)	569 (3940)	546 (3780)	b	289
81-C	--	0	11.1 (76.9)	435 (3010)	430 (2980)	h	288
82	Q	7.1	11.6 (80.4)	556 (3050)	528 (3680)	h	287

In Table 6, composites using polymer blends of nylon h and nylon b were made. One blend, example 85, was made by preparing a clay concentrate in nylon h, such as control sample 83-C, and then blending the concentrate with a second polymer, such as b.

5 The second blend, example 86, was made by preparing a clay concentrate of nylon b, and blending in the nylon h. The composites were processed using a ZSK twin screw extruder.

Table 6
Varying Nylon Blend

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Nylon Type	Melt Temp. (°C)
83-C	Q	20.1	7.77 (53.8)	824 (5710)	722 (5000)	h	280
84	Q	7.1	11.9 (82.5)	612 (4240)	547 (3790)	h	281
85	Q	7.3	12.2 (84.5)	593 (4110)	549 (3800)	b/h ¹	281
86	Q	5.9	12.3 (85.2)	613 (4250)	529 (3670)	h/b ²	281
87	Q	6.3	12.3 (85.2)	588 (4070)	540 (3740)	b	282

¹The weight ratio of nylon blend b/h was 70/30.

²The weight ratio of nylon blend h/b was 70/30.

-41-

In Table 7, a concentrate of the treated clay and a polymer other than a polyamide is let down, or diluted with the nylon h. The controls are a mixture of the polymer neat and nylon h.

Table 7
Clay/Other Polymer Concentrate Let Down With Nylon

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Other Polymer (%)	Melt Temp. (°C)
88-C	--	0	9.49 (65.7)	372 (2580)	322 (2230)	12.7 ¹ 288	
89	2	6.5	9.96 (68.9)	452 (3130)	411 (2840)	12.7 ¹ 287	
90-C	--	0	10.4 (71.6)	393 (2720)	370 (2560)	7.0 ¹	287
91	2	7.1	10.5 (72.8)	472 (3260)	451 (3120)	7.0 ¹	283
92-C	--	0	8.75 (60.6)	352 (2440)	319 (2210)	15.4 ² 288	
93	2	7.4	9.67 (66.9)	436 (3020)	437 (3020)	15.4 ² 281	
94-C	--	0	9.52 (65.9)	380 (2630)	354 (2450)	9.7 ²	287
95	2	7.2	10.5 (72.8)	515 (3560)	471 (3260)	9.7 ²	281

¹The other polymer used was Iotek 971 ionomer.

²The other polymer used was ATX 320 acid terpolymer.

The runs in Table 8 vary the feed points for processing the nylon with the treated clay. The clay was fed into the ZSK twin screw extruder at the throat or downstream of the throat. The nylon used was a copolymer of 80% nylon 6,6 and 20% nylon 6.

Table 8
Varying Feed Point of Nylon for Processing

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
96-C	--	0	10.5 (72.8)	376 (2600)	286 (1980)	251
97	Q	5.4	10.7 (73.4)	468 (3240)	391 (2710)	251 ¹
98	Q	5.5	10.8 (74.5)	489 (3370)	370 (2560)	249 ²
99	Q	2.9	10.5 (72.7)	467 (3230)	378 (2620)	250 ³
100	Q	3.4	10.9 (75.2)	490 (3390)	377 (2610)	250 ⁴
101	Q	4.7	10.6 (73.6)	500 (3460)	375 (2600)	250 ⁵
102	Q	4.8	10.8 (75.1)	521 (3620)	406 (2810)	250 ⁶
103	Q	3.8	10.6 (73.4)	463 (3200)	350 (2420)	256 ⁷
104	Q	4.2	10.8 (74.7)	490 (3390)	359 (2480)	250 ⁸

¹ Nylon fed in throat of ZSK twin screw extruder.

² Second pass of run 97.

³ Nylon fed downstream of throat of extruder.

⁴ Second pass of run 99.

⁵ Nylon fed downstream of throat of extruder.

⁶ Second pass of run 101.

⁷ Nylon fed in throat of extruder.

⁸ Second pass of run 103.

In Table 9, composites are prepared from eight (8) different quaternary ammonium/ammonium blend-treated silicates. The composites are processed using a ZSK twin screw extruder. Taking into account the standard deviations of the tensile strength measurements, all of the samples show an increase in tensile modulus and flex modulus without a decrease in tensile strength. Samples 125 through 135 show the effect of varying the nylon type.

Table 9
Ammonium Blend-Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
105-C*	--	0	11.4 (78.6)	455 (3140)	450 (3100)	259
106*	GG	5.6	13.7 (94.5)	596 (4110)	578 (3990)	263
107-C	--	0	11.5 (79.3)	463 (3190)	429 (2960)	286
108	HH	1.3	11.8 (81.4)	476 (3280)	472 (3260)	285
109	HH	5.2	11.4 ¹ 552 (78.7)	545 (3810)	286 (3760)	
110	II	2.3	12.0 (82.8)	465 (3210)	429 (2960)	286
111	II	5.6	11.8 (81.4)	560 (3860)	545 (3760)	285
112	JJ	2.0	11.9 (82.1)	470 (3240)	483 (3330)	285
113	JJ	4.3	11.5 (79.3)	542 (3740)	537 (3700)	286

*Runs 105 and 106 use nylon f.
¹ Standard deviation of ±0.85.

Table 9, Continued
Ammonium Blend-Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
114-C	--	0	11.2 (77.2)	411 (2830)	405 (2790)	287
115	KK	2.8	11.5 (79.3)	470 (3240)	475 (3280)	287
116	KK	6.2	10.9 ¹ 494 (75.2)	536 (3410)	288 (3700)	
117	LL	3.4	11.6 (80.0)	500 (3450)	510 (3520)	288
118	LL	6.7	11.0 ² 544 (75.9)	542 (3750)	288 (3740)	
119	MM	3.2	11.5 (79.3)	480 (3310)	497 (3430)	287
120	MM	6.5	11.0 ³ 529 (75.9)	540 (3670)	288 (3720)	
121-C	--	0	11.6 (80.0)	427 (2940)	466 (3210)	282
122	NN	3.5	12.6 (86.9)	522 (3600)	568 (3920)	282
123	NN	6.5	12.6 (86.9)	572 (3940)	623 (4300)	282
124	NN	8.4	11.3 ⁴ 650 (77.9)	664 (4480)	283 (4580)	

¹ Standard Deviation of ± 1.22

² Standard Deviation of ± 0.24

³ Standard Deviation of ± 0.49

⁴ Standard Deviation of ± 0.60

Table 9, Continued
Ammonium Blend-Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
125-C ¹	--	0	11.7 (80.7)	488 (3370)	481 (3320)	268
126 ¹	NN	8.1	11.9 (82.1)	640 (4410)	598 (4120)	265
127-C ²	--	0	11.4 (78.6)	482 (3320)	454 (3130)	285
128 ²	NN	8.1	11.7 (80.7)	658 (4540)	618 (4260)	315
129-C ³	--	0	11.4 (78.6)	434 (2990)	441 (3040)	262
130 ³	NN	1.7	12.1 (83.4)	491 (3390)	506 (3490)	270
131 ³	NN	4.0	12.8 (88.3)	567 (3910)	557 (3840)	276
132-C ⁴	--	0	11.8 (81.4)	434 (2990)	439 (3030)	269
133 ⁴	NN	2.2	12.1 (83.4)	480 (3310)	509 (3510)	276
134 ⁴	NN	4.3	12.5 (86.2)	580 (4000)	557 (3840)	282
135 ⁴	NN	6.8	12.4 (85.5)	635 (4380)	643 (4430)	286

- ¹ Samples use nylon a.
² Samples use nylon c.
³ Samples use nylon a.
⁴ Samples use nylon e.

-49-

In Table 10, composites are prepared from six (6) different tertiary ammonium-treated silicates. The composites are processed using a ZSK twin screw extruder. Taking into effect the standard deviation of the tensile strength measurements, all of the samples show an increase in tensile modulus and flex modulus without a decrease in tensile strength.

Table 10
Tertiary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
136-C	--	0	12.1 (83.4)	443 (3060)	456 (3140)	296
137	OO	5.4	13.0 (89.7)	591 (4080)	568 (3920)	297
138	PP	4.9	12.9 (89.0)	588 (4060)	545 (3760)	297
139	QQ	4.1	12.8 (88.3)	573 (3950)	549 (3790)	296
140	RR	4.4	12.4 (85.5)	533 (3680)	518 (3570)	297
141	SS	3.1	11.9 ¹ 488 (82.1)	499 (3370)	296 (3440)	
142-C	--	0	11.6 (80.0)	445 (3070)	436 (3010)	280
143	TT	2.7	12.2 (84.1)	508 (3500)	497 (3430)	283
144	TT	6.2	12.3 (84.8)	587 (4050)	571 (3940)	287

¹ Standard Deviation of ± 1.1

-51-

In Table 11, samples 147, 150, 152, 154 and 156 are subjected to solid state polymerization. A dramatic improvement is noted in the tensile strength and elongation.

Table 11
Process Variations

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	% Elongation	Melt Temp. (°C)
145-C	--	0	11.7 (80.7)	488 (3370)	481 (3320)	29.4	268
146	NN	8.1	11.9 (82.1)	640 (4410)	598 (4120)	2.5	265
147 ¹	NN	8.1	14.2 (97.9)	689 (4750)	630 (4340)	3.2	265
148-C	--	0	11.4 (78.6)	482 (3320)	454 (3130)	33.8	285
149	NN	8.1	11.7 (80.7)	658 (4540)	618 (4260)	2.1	315
150 ¹	NN	8.1	13.9 (95.9)	681 (4700)	663 (4570)	2.9	315
151-C	--	0	11.4 (78.6)	421 (2910)	430 (2980)	38.8	275
152 ¹ -C	--	0	11.5 (79.7)	428 (2970)	446 (3090)	40.4	275
153	NN	5.1	13.6 (94.2)	620 (4300)	569 (3940)	12.7	--
154 ¹	NN	5.1	13.7 (94.9)	536 (3710)	574 (3980)	10.7	--
155 ²	NN	3.9	12.7 (88.0)	560 (3880)	538 (3730)	5.8	280
156 ^{1,2}	NN	3.9	12.9 (89.4)	524 (3630)	513 (3560)	20.5	280

¹ Subjected to solid state polymerization at about 220°C for about 3 to 4 h.

² Stabilized with 0.25% Irganox LC21FF stabilizer sold by Ciba-Geigy Co.

Samples 145 to 147 and 151 to 156 use nylon a.

Samples 148 to 150 use nylon c.

-53-

IN-SITU POLYMERIZATION OF NYLON NANOCOMPOSITES

Process Description:

5 In-situ polymerization holds great promise for improving clay dispersion and enhancing the strength of the silicate-nylon interface over that obtained by melt compounding. Efficient reinforcement comprising more than 20% increase in modulus has been found for a nanocomposite containing only 0.1% by weight nano-silicate. Silane may be added to the reactor feed to improve interfacial bonding in the final nanocomposite.

10 Polyamide nanocomposite compositions may be formed by a process comprising forming an aqueous mixture of a treated silicate material and a polyamide monomer, treating the mixture to polymerize the polyamide monomer, and dissociating at least about 50% of the silicate material to form a polyamide nanocomposite composition.

15 In a specific embodiment, layered (montmorillonite, saponite, hectorite, laponite) and chain-like (sepiolite) silicates may be incorporated into nylon 6,6 and nylon 6,6/6 copolymers by exfoliating and dispersing the clay in the hexamethylene adipamide (HMA) nylon 6,6 salt solution prior to polymerization. Nylon 6,6/6 copolymers may be produced by including a component of epsilon-caprolactam in the monomer feed. The process has been demonstrated in both laboratory and pilot (250 pound (113 kg)) scale autoclaves.

20 In an alternative embodiment directed towards the preparation of copolymers, the silicates may be pre-dispersed in the caprolactam component prior to its addition to the salt solution. Alternatively, concentrates may be made in nylon 6 or in its precursor caprolactam solution, preferably with the addition of a peptizer, for later addition to the nylon 6,6 polymerization mixture. Low molecular weight liquid polyamides may be used as carriers for the nanoclay. Concentrates of
25 the nanoclay exfoliated in these carriers by high shear homogenization may be added later in the nylon 6,6 polymerization cycle after the aqueous ionic environment is driven off.

-54-

The following parameters may affect the performance of the process:

- a. Prior dispersion of the clay in water, or use of wet never-dried clay, before introduction to the polymerization mixture;
- b. Application of high shear, ultrasonic energy or venturi cavitation flow to enhance exfoliation of the clay layers prior to polymerization;
- c. Salt concentration;
- d. pH;
- e. Diamine/acid ratio in the HMA salt solution;
- f. Ion exchange of cations on the clay surface to alter its hydrophobicity and reactivity or physical interaction with the nylon polymer matrix;
- g. Clay concentration;
- h. Type of silicate;
- i. Molecular weight of the nylon at the point clay is added to the polymerization; and
- j. Composition of the nylon polymer/copolymer.

It may be preferable to perform the process with a "diamine spike", i.e., a higher molar concentration of hexamethylene diamine (HMD) than adipic acid in the mixture to counter any acidity due to the clay or its treatment, as well as to compensate for the loss of HMD by vaporization during the polymerization cycles. The resulting higher viscosity of the polymerized melt indicates a greater molecular weight build in the polymer matrix.

Silicate materials

Certain mineral types are preferable for use in the in-situ polymerization process, including synthetic Laponite, commercially available from SCP under the trade name Laponite®, hectorite, sepiolite, saponite, and montmorillonite at various points in the reaction cycle. It has been found to be preferable to first achieve a good dispersion of the exfoliated silicate layers in water prior to contact with the salt solution. In this regard it may be useful to start with a never-dried aqueous dispersion or aqueous suspension instead of dry silicate. Alternatively, dry silicate may be hydrated prior to its participation in the polymerization process. Silicate may be dispersed through high shear

-55-

homogenization or cavitation generated ultrasonically or by throttling the aqueous suspension through a venturi tube or other methods known in the art.

The silicate material may be organically modified to produce a stronger interface with the nylon matrix phase of the final nanocomposite. Such organoclays are more hydrophobic than the
5 pristine minerals and so may not form stable colloidal dispersions in water or in the nylon 6,6 salt solution. However, as in the melt compounding approach of the earlier patent application, polymer can intercalate the layered clay structure later in the polymerization cycle after the aqueous phase has been largely removed by vaporization. In fact, its lower molecular weight should actually enhance the rate of intercalation, leading to a more complete state of layer exfoliation and higher
10 reinforcement of the final composite by the resulting smaller particle thicknesses than is obtained by direct melt compounding with a pre-polymerized nylon resin.

Non-ionic conditions

In an embodiment designed to completely avoid an ionic environment, the silicate material may be added later in the polymerization cycle after the salt has been converted to oligomers or low
15 molecular weight polymers. An alternate approach to avoiding ionic effects is to start the process with molten anhydrous salt in place of the salt solution.

Peptizers

In order to avoid gelling, it may be preferable to limit concentration to 2% or possibly up to 4% of the other minerals. Higher concentrations up to about twice these limits may be feasible
20 when a peptizer is also present in the mixture. These contain phosphate ions which may retard the buildup of structure in aqueous suspensions. The phosphates also act as buffers to control pH, which may also be desirable in achieving a high degree of clay dispersion.

Examples:

Four clay types received from Southern Clay Products, Inc., Gonzales, TX - Mineral
25 Colloids BP and MO along with Claytone types AF and APA, were dispersed in water, a 70% solution of caprolactam in water and a 50% aqueous solution of hexamethylene adipamide (HMA) at 1% using a Dispermat mixer running at 50 cycle/sec for 60 seconds. Of these four clays, only the dispersion of BP in water was stable. The high shear mixing is preferred. An Omni mixer is an example of a commercially available machine capable of achieving high shear mixing.

-56-

It was found that aminolauric acid clay treatment provides improved stability to the colloidal clay suspension in salt solution. Indeed, a macroscopically uniform product of 4% aminolauric acid treated montmorillonite was polymerized into nylon 6,6 in a lab autoclave. However, transmission electron microscopy (TEM) and wide angle x-ray scattering (WAXS) revealed that the silicate of this composite is not fully exfoliated. The mechanical properties of injection molded specimens were not enhanced by the presence of the clay.

Foaming was experienced during in-situ polymerization in a lab autoclave with tallow-based (e.g., dimethyl-dihydrogenated tallow ammonium (2M2HT)) organoclay, while untreated (pristine) sodium and calcium montmorillonites did not exfoliate, according to clumps visible by optical microscopy. Use of tertiary ammonium silicate treatment rather than their quaternary counterparts were found to reduce foaming.

A 97.5/2.5 nylon 6/6,6 copolymer was polymerized in the presence of 4% by weight 12-aminolauric acid organomontmorillonite. The product displayed considerably enhanced toughness and ductility over the nylon 6,6 homopolymer nanocomposite. Optical microscopy indicated the absence of any micron-sized clay residue, suggesting a higher degree of clay delamination than for the earlier homopolymer. This was confirmed by transmission electron microscopy (TEM). Injection molded properties of this sample were high, showing a 25% increase in tensile modulus and 50% increase in yield strength, with only about 1% silicate on a volume basis - a high reinforcement efficiency.

Alkoxy-modified organoclays comprising the more polar ammonium ions synthesized from alkoxy-functional Jeffamines were observed to produce more stable colloidal suspensions in mixed HMA/caprolactam solutions. In-situ polymerization was successfully performed with an ethoxy-modified montmorillonite. Initially, temperature was kept low ($< 260^{\circ}\text{C}$) to safeguard against degradation of the clay coating. Smaller test tube sized polymerizations were performed without stirring in a Parr reactor over a range in ethylene oxide / propylene oxide sequencing on the ammonium cation of the treated montmorillonite. WAXS measurements showed the same degree of polymer intercalation into the silicate structure as in samples made with stirring in a lab autoclave. Coating compositions allowed the nylon 6,6 content to be raised as high as 12% without obstructing the silicate intercalation.

-57-

One polypropylene oxide quat produced a particularly stable colloidal suspension in a 50/50 mixture of nylon 6,6 salt solution and caprolactam solution that did not phase separate for several days at room temperature. In contrast, pristine sodium montmorillonite suspensions were found not to be stable at room temperature across a range of HMA/caprolactam mixture compositions, though in-situ polymerization of straight nylon 6 nanocomposite from caprolactam solution comprising Gelwhite pristine Ca-montmorillonite supplied by Southern Clay Products, Inc. produced a smooth-flowing concentrate that could later be let down into nylon 6,6 to form a blended nanocomposite.

Gelwhite L nanocomposites of 5, 10 and 15% concentration in nylon 6 prepared in a lab autoclave were let down in nylon 6,6 by adding them to the hexamethylene adipamide salt solution prior to nylon 6,6 polymerization. Although the resulting blend fibers were bright and smooth, indicating the absence of clay clumps, no improvement of physical properties was noted.

Hydration of silicates

It was discovered that when montmorillonite is fully pre-hydrated, either as a never-dried slurry or by first completely suspending dry clay in water, it forms a more stable colloidal suspension in hexamethylene adipamide salt solution. The following types were found to produce stable 3% colloidal suspensions in water following high shear mixing with an Omni homogenizer: Gelwhite H and Gelwhite L (sodium-exchanged Ca-montmorillonite), Mineral Colloid BP (pristine Na-montmorillonite), poly(propylene oxide) treated montmorillonite, and a hydroxy-terminated poly(ethylene oxide / propylene oxide) copolymer treated montmorillonite. 72 hours after adding salt solution to the water slurries at a level corresponding to 4% clay in the final nanocomposite the following types remained in suspension: Gelwhites H and L, Mineral Colloid BP and certain of the polyether organoclays. The other slurries were stable for at least one hour. Any clays that would not hydrate in water were also found not go into suspension when nylon salt was added.

Suspensions of the following clays made by the above technique were then polymerized without mixing in test tubes using a Parr reactor: Gelwhites H and L, Mineral Colloid BP, and certain of the polyether organoclays. However, the silicate layer d-spacing measured by WAXS in the resulting nanocomposite was still low (13.9 - 14.3 Å), indicating little polymer intercalation of at least a portion of the clay. However, the spacing is larger than found in the as-received Mineral

-58-

Colloid BP Na-montmorillonite. Addition of carboxymethyl cellulose (CMC) was investigated to hold the clay surfaces apart until a low molecular weight polymer is formed.

Nylon 6 examples

By using a modified nylon 6,6 two hour batch polymerization cycle, nylon 6 nanocomposites were prepared in-situ from a water solution of caprolactam containing a range of pristine nanoclays, including Ca-montmorillonite, Na-montmorillonite, laponite RD synthetic hectorite and attapulgite. The laponite appeared to disperse most readily, showing no peaks in the WAXS spectrum of the resulting nanocomposite. The relative viscosity (RV) of the resulting nanocomposite was equal to the neat control and its translucency indicated good clay dispersion. A 4-9°C rise in recrystallization temperature vs. the control indicates that the nanoparticles are altering the crystal structure of the nylon matrix in the manner of nucleating agents.

sample ID	Nanoclay %, type	RV	DSC m.p.(°C)	DSC recryst.T(°C)
5420078	(nylon-6 control)	28.1	212.1	143.3
5420079	3.0% GEL WHITE H	26.3	212.1	151.1
5420080	2.0% GEL WHITE H	23.2	212.2	150.1
5420081	1.0% GEL WHITE H	28.4	209.9	150.8
5420082	0.5% GEL WHITE H	25.5	209.7	149.6
5420083	2.0% LAPONITE RD	-	210.5	150.7
5420084	2.0% GEL WHITE L	24.2	209.2	152.4
5420085	2.0% ATTAPULGITE	28.4	211.2	147.4
5420086	2.0% Mineral Colloid BP(Na Montmorillonite)	25.5	209.5	152.4

It is thus seen that the presence of the silicate does not appear to affect the polymerization of the nylon. Tensile data on nylon 6 nanocomposite film samples prepared by hot pressing autoclave extrudate between flat plates show a general increase in stiffness with increasing concentration of Gelwhite H pristine Ca-montmorillonite, while tensile strength and elongation are somewhat reduced. The modulus of composites made from Mineral Colloid BP pristine Na-montmorillonite was found to be significantly (40%) higher than any of the other clays tested.

-59-

Sample	Clay Type	Clay Conc wt %	Yield Stgth kpsi	Break Stgth kpsi	Ult. Elong. %	1% Secant Mod., kpsi
5420078	(control)	0	0.68	5.0	40.	126
5420079	Gelwhite-H	3	0.66	4.0	7	156
5420080	Gelwhite-H	2	0.58	3.0	5	130
5420081	Gelwhite-H	1	0.63	3.6	6.8	100
5420083	Laponite-RD	2	0.6	2.0	3.6	134
5420084	Gelwhite-L	2	0.50	3.0		116
5420086	Min Col-BP	2	0.57	3.0	3	180

The above experiment was repeated at 1% and 2.5% mineral with the addition of Laponite B mineral as an additional run. Addition of tetrasodium pyrophosphate (TSPP) peptizer to the Gelwhite H sample during homogenization aided in forming a dispersion. The resulting fiber was delustered in comparison to the other candidates. All 1% nanocomposites demonstrated a 10°C increase in recrystallization temperature.

Experiments were conducted on intercalation of layered silicate with molten nylon of low molecular weight into pristine Ca-montmorillonite.

Nylon 6 nanocomposite fiber spun from the polymerization autoclave and comprising 2.5% laponite RD silicate showed a measure of electrical conductivity under high voltage testing. At 5% and 10% concentrations, the melt viscosity was so high that the nanocomposite melt could not be discharged from the autoclave.

Additional mechanical results were obtained on nylon 6 fiber: Gelwhite L and Laponite RD are preferred over Mineral Colloid BP, Gelwhite H, Laponite B and attapulgit for improving modulus without loss in tenacity and elongation. Both spun and drawn yarns were bright and free of nubs.

nanoclay	RV	T _c (°C)	tenacity (g/d)	elong (%)	modulus (g/d)
control	39	147.2	2.5	97.3	10.7
control	38	148.4	2.5	71.7	10.5
LAPONITE RD					
2.5%	54	154.1	1.8	56.4	12.7
1.0%	34	159.6	2.4	84.2	14.9
0.5%	43	157.0	2.4	66.8	11.7
GELWHITE L					

-60-

nanoclay	RV	T _c (°C)	tenacity (g/d)	elong (%)	modulus (g/d)
2.5%	32	154.7	2.4	70.9	13.2
1.0%	35	156.2	2.5	87.1	15.0
0.5%	40	159.1	2.3	67.8	15.0

All of the clay types did show nucleating activity. The above experiments were repeated in part at the 0.5% and 1.0% clay levels, with the clays predispersed in a 70% caprolactam solution. The fourth cycle of the standard nylon 6,6 polymerization cycle was extended from 30 to 60 minutes.

Nanoclay	RV	DSC recrystemp (°C)	Testing of drawn yarn			
			denier	tenacity	elong	mod
none (control)	40.1	145.6	106	2.44	8.60	6.7
0.5% GEL WHITE L	36.6	148.9	99	2.70	8.52	10.6
1.0% GEL WHITE L	35.9	154.6	89	2.14	5.75	11.6
0.5% LAPONITE RD	41.5	151.8	100	2.68	8.62	9.8
1.0% LAPONITE RD	44.6	152.9	93	2.45	8.62	6.8

Nanoclay	RV	DSC recrystemp (°C)	Testing of spun yarn			
			denier	tenacity	elong	mod
none (control)	40.1	145.6	303	0.88	437	4.57
0.5% GEL WHITE L	36.6	148.9	272	1.02	436	4.52
1.0% GEL WHITE L	35.9	154.6	254	0.89	397	5.16
0.5% LAPONITE RD	41.5	151.8	291	1.04	445	4.25
1.0% LAPONITE RD	44.6	152.9	274	0.92	445	4.73

These nanoclays produce enhanced modulus at the 0.5% and 1.0% levels, along with some increase in tenacity at 0.5%. They were also seen to be efficient nucleating agents for nylon 6. However, they also produced higher gel levels, showing HPLC fluorescence numbers of around 100 ppm vs. 0-1 ppm for the nylon control.

Nylon 6,6 examples

Nylon 6,6 nanocomposites may be polymerized by standard industrial procedures as described in the "Nylon Plastics Handbook" (Melvin I. Kohan, Hanser Publishers, Munich, 1995, pp. 17-23).

5 Gelwhite L may be made into a concentrate of up to 20% in nylon 6 via in-situ polymerization (with Tamol 850, a sodium polymethacrylate from Rohm and Haas Company, to aid clay dispersion). These concentrates were extruded at the end of the third cycle of the standard polymerization process and given a water quench. The nanocomposites were pulverized and added back to a nylon 6,6 polymerization, either to the salt solution at the beginning of the process or later
10 after the batch achieved a temperature of 220°C. The latter technique generated gels, and neither resulted in any enhancement to the mechanical properties of spun fiber.

A never-dried slurry of an ion exchanged Ca-montmorillonite in which the Ca^{2+} ions have all been exchanged for Na^+ , and containing polyacrylate as peptizer was also polymerized into nylon 6,6 fiber at 1% concentration, but with no improvement in yarn properties. Melt viscosity was high,
15 but spinnable. The resulting yarn appearance was smooth, but delustered. The Ca^{2+} mined ores are attractive for fiber applications because of their whiter color. However, the aspect ratio of their exfoliated platelets is known to be lower than those from mined Na-montmorillonite.

If the clay dispersion in nylon 6,6 salt solution is allowed to age for even a few hours, it begins to coagulate. Polymerization of a one-day old dispersion resulted in a lower RV of the nylon
20 6,6.

Silicate concentrate carrier solutions

An alternative embodiment for the preparation of silicate / polyamide nanocomposites via in-situ polymerization is to pre-disperse the clay at high concentration in a carrier (as a "concentrate") for addition to the polymerization vessel. For example, it was found possible to disperse Gelwhite L
25 at concentrations of 10-30% in an aqueous solution comprising 25% (based on the weight of the clay component) of a solution of 70% epsilon caprolactam in water and 1%-5% Tamol 850 dispersing agent. These dispersions remained stable for over three weeks at room temperature. Without the dispersing agent, the dispersion of Gelwhite L at concentrations of or above 10% become unpourable gels. An advantage to the use of these clay concentrates is their possible

-62-

addition to the reaction mixture later in the polymerization cycle after the ionic aqueous environment has largely been dissipated through vaporization, thus reducing the chances for flocculation. In this example, the dispersion was injected into a nylon 6,6 batch polymerization when the temperature was in the range of 220°C-235°C. The resulting fibers contained nubs which fluoresced under UV light, indicating the presence of gel. Fiber properties were consequently not improved over the nylon control.

In another example of the above technique, Laponite RD could be dispersed at a high concentration of 10% in a 70% solution of caprolactam in water by combining 3% Tamol® 850 with 100% ethylene glycol, both concentrations based on the weight of the clay.

Tetrasodium pyrophosphate (TSPP) and carboxymethyl cellulose (CMC) were found to not be effective peptizers to stabilize montmorillonite suspensions after addition to the nylon 6,6 salt solution, according to WAXS data.

Tamol® dispersing agent was effective in polymerizing 1.5-2% nanocomposites of Mineral Colloid BP in nylon blends comprising 20-30% nylon 6 in nylon 6,6 from aqueous mixtures of caprolactam and hexamethylene adipamide. However, the viscosity of the 2% nanocomposite was so high that it could not be extruded from the reactor. The copolymer composition is attractive because the lower salt concentration reduces clay flocculation while the caprolactam component enhances intercalation of the clay structure, leading to more efficient exfoliation.

Potassium tripolyphosphate (KTPP) has been found to be an effective peptizer for nanosilicates in nylon 6,6 salt solution. It is also believed to suppress gel formation. Spun and drawn fibers prepared by injecting stabilized Gelwhite slurry later in the nylon 6,6 polymerization cycle were bright and gel-free, unlike the nubs and fluorescent gels routinely obtained with TSPP and Tamol® 850 peptizers. Fiber containing 0.3% nanoclay retained its matrix properties.

NBP ID #	KTPP (% of clay)	HPLC fluo. (ppm indole)	Tenacity (g/d)	Elong (%)	Modulus (g/d)
5820338 (control)	-	-	3.28	86.0	19.3
5820402 (control)	-	-	3.20	89.0	23.4
5695896	TAMOL850	102	2.98	89.7	15.2

-63-

NBP ID #	KTPP (% of clay)	HPLC fluo. (ppm indole)	Tenacity (g/d)	Elong (%)	Modulus (g/d)
5695894	TAMOL850	88	2.90	51.5	13.9
5820336	4	0	3.00	81.7	20.0
5820335	2	0	3.20	80.0	19.6
5820348	1	11	3.22	85.7	19.9
5820349	0.5	1			
5820350*	1		3.01	75.1	18.2
5820351*	0.5		3.10	86.2	16.6

Note: A 10% GEL WHITE L slurry in 70% aqueous caprolactam solution was prepared with various amounts of KTPP. In 5820350* and 5820351*, however, GEL WHITE L/caprolactam solution was kept at 1/1.

5 Fiber comprising 0.6% Mineral Colloid BP, 1% KTPP based on the clay weight and a small amount of caprolactam also appeared bright with only minor nub generation.

Many quaternary ammonium halide salts, such as those used in the organomontmorillonites lack the thermal stability required to withstand nylon 6,6 polymerization temperatures of 280-300°C. A lauryl-dimethyl-3-sulfopropyl betaine (Ralufon DL from Raschip Corp.) with higher
10 temperature stability successfully intercalated Gelwhite L pristine Ca-montmorillonite at 1% concentration in 70% caprolactam solution which, when injected late in the nylon 6,6 polymerization cycle, produced a nylon 6,6 fiber at 0.3% mineral concentration with good luster and absence of gel, along with acceptable mechanical properties.

2% nanocomposites of Mineral Colloid BP, aminolauric acid and (2-ethylhexyldimethyl
15 hydrogenated tallow)modified montmorillonite, were made by infiltration of molten hexamethylene adipamide salt and low (9-10) RV nylon 6,6 polymer, in order to avoid exposure to the ionic environment of the salt solution. WAXS data show the latter approach to improve polymer intercalation in opening up the clay structure.

20 Nylon 6,6 nanocomposites comprising 1% nanoclay were prepared from never-dried aqueous suspensions, with the exception of dry Gel-White H which had to be re-dispersed in water. The pre-dispersions are further mixed under high shear with an Omni homogenizer for 10 minutes after introduction to the salt solution.

-64-

Sample No.	Clay type	Additive	Clay Conc.	Intrinsic Viscosity	[COOH]	[NH ₂]	Mw	Mv/Mw
8515	Na-mont.	0.9% CMC	1.4 %	0.745	149.1	65.5	17000 (Mv)	
8517	Na-mont.	-	2.0 %	0.769	114.4	43.5	25300	0.70
8518	Na-mont.	-	1.0 %	0.902	121.3	37.6	25200	0.86
				0.896	124.8	38.8	24500	0.87
8519	aminolauric acid-mont.	-	1.0 %	0.942	142.1	35.2	22600	1.01
8520	aminolauric acid-mont.	-	2.0 %					
8521	Gel-White H	-	1.0 %	0.971	106.6	41.7	27000	0.88
8522	Ca-mont.	-	1.0 %					

All of the above clays were obtained from SCP. The Ca-montmorillonite slurry was ion exchanged with sodium ions and also contained an acrylic peptizer.

5 Samples 8515, 8517 and 8520 could not be extruded out of the polymerization autoclave due to their high melt viscosity, suggesting a significant degree of clay exfoliation despite the presence of a residual WAXS peak at 14.4Å. The greater breadth of the peak does indicate that the original lamina stacks in the clay have been reduced somewhat in thickness. A nylon 6,6 nanocomposite comprising 1% nanoclay from Na-montmorillonite never-dried slurry showed high reinforcement efficiency with a 15% increase in tensile modulus. Sample 8522 was injection molded into tensile test bars which showed a 15% increase in modulus from 435 to 500 kpsi, a highly efficient reinforcement from the small amount of clay present.

The presence of clay does not appear to have any significant effect on the molecular weight of the polymer formed, or its distribution. The presence of CMC in Sample No. 8515 reduces molecular weight, as expected.

15 Five replicate runs of carpet and industrial tire cord fibers modified with 0.5% and 1.0% Gelwhite L were prepared in a small autoclave from a 10% clay pre-dispersion in 70% aqueous caprolactam solution containing 1% each of KTPP and Tamol 850 based on the weight of the clay. The clay slurry was injected into a nylon 6,6 polymerization during the second cycle of the process at 235°C. Modulus increased by 10-20% in the spun fibers at both concentration levels, although this advantage was retained after drawing only in the carpet fiber at the lower concentration level.

-65-

Tenacity and elongation of both spun and drawn fibers of both types showed small decreases. It was later shown to be preferable to omit the Tamol ingredient in this particular formulation.

A significant level of nano-reinforcement was achieved in injection molded nylon 6,6 nanocomposites made by in-situ polymerization in a 250-pound (113 kg) batch with a very low mineral concentration. A tensile modulus enhancement of 90 kpsi (20%) over neat nylon due to incorporation of only 0.072% mineral content by weight of laponite RD synthetic hectorite represents ten times the maximum benefit that could be anticipated from classical reinforcement mechanisms. Very small crystallite size, indicating nucleation, was detected in these nanocomposites by optical microscopy through crossed polarizers.

Pristine sepiolite, a chain-like silicate, has been demonstrated to be equally effective as montmorillonite or hectorite for nylon fiber reinforcement via in-situ polymerization. At 0.1% concentration it provides a high draw capability and enhanced mechanical properties. At 6.5 draw ratio the following fiber properties were obtained vs. a neat nylon control fiber: 84 vs. 76 g/d modulus, 10.2 vs. 9.1 g/d tenacity and 12.3 vs. 10.4% elongation to fail. The nylon matrix RV was equivalent to the neat nylon control.

Sepiolite (1%) increased flex modulus by 13% in nylon 6,6 polymerized in a lab autoclave. In scale-up to the 250-pound autoclave (113 kg), however, the sepiolite nanocomposites did not demonstrate as great an improvement on the nanocomposite as in the smaller scale experiments. Injection moldings containing 0.09% by weight pristine sepiolite showed lower reinforcement than the corresponding laponite materials. Tensile strength still increased significantly from 11.1 to 12.0 kpsi in comparison to the unreinforced nylon 6,6 control. The increase in modulus was only a modest 6%, while elongation still reached 30% strain. As with laponite, the presence of the sepiolite mineral during the nylon polymerization had no effect on the nylon polymer, which registered an RV of 42 and acid/amine end group concentrations of 72/52.4. An advantage of sepiolite is that it can be effectively dispersed directly into the HMA salt solution without the need for making a predispersion in water.

Silane, particularly aminopropyltriethoxysilane, may be incorporated into polyamides such as nylon 6,6 by addition to the salt solution along with the nanoclay prior to polymerization. At low levels (0.12-0.25%), it provided no significant benefit to the properties of the resulting

-66-

nanocomposite fibers also comprising low (0.1%) levels of nanoclay. However, at the higher concentrations of both silane (up to 0.5%) and nanoclay (up to 2%) used for injection molding, it does serve to enhance the nanocomposite ductility. Apparently the interfacial strengthening usually attributed to silanes in melt compounded systems can also be effective via in-situ polymerization.

5 On the other hand, in the absence of the silicate the silane alone showed some reinforcing potential of its own in drawn fiber.

The higher aspect ratio reinforcements in general produce higher properties in fiber drawn from in-situ polymerized nylon 6,6 nanocomposites. Thus, montmorillonite and hectorite are more effective than laponite B, which in turn is more effective than laponite RD.

10 Crystallinity is increased slightly and recrystallization temperatures generally increased (by up to 8°C) through the incorporation of nanoclay during polymerization. Sepiolite, saponite and, to a lesser extent, hectorite are the most efficient nanosilicate nucleators.

Further examples of fibers spun and drawn from in-situ polymerized nylon 6,6 nanocomposites at the pilot plant scale comprise montmorillonite, hectorite and laponite B, both
15 pristine and ion exchanged with ammonium cations. Increases of 15% in modulus and tenacity were achieved along with a 30% increase in creep resistance at a low mineral concentration of only 0.1% by weight that would be significant for tire cord applications. Higher increases of up to 30% in modulus with 10% in tenacity were observed at the bench scale.

Of particular note, the 2% secant modulus of 0.1% pristine hectorite nanocomposite drawn
20 carpet yarn of 16.6 g/denier was 44% higher than the 11.7 g/denier control yarn produced in the same test and drawn to the same denier. Elongation to fail was equivalent to the control, while tenacity was enhanced slightly. The good performance of this nanocomposite may be attributed to pre-dispersion of the silicate in a minor caprolactam component of the formulation.

Dihydroxyethyl octadecylammonium is the preferred cation exchanged onto the
25 phyllosilicate minerals for in-situ polymerization in nylon 6,6. A nanocomposite in-situ polymerized with either 0.2 and 0.4% of montmorillonite previously treated with this cation showed improved appearance retention in carpet walk testing. Due to their less hydrophilic nature, organoclays are pre-dispersed at up to 5% concentration directly in nylon salt solution rather than in pure water, as is preferred for the pristine minerals.

-67-

A slight inhibition of nylon 6,6 polymerization that may occur at higher silicate concentrations (e.g., 2%) may be overcome by increasing reactor residence time in the finishing cycle by about 30%.

Enhanced modulus along with a slightly reduced ductility indicate a better nanoparticle dispersion resulting from the application of ultrasonic energy to the initial clay slurry.

The ideal mineral concentration for fiber spinning appears to be below about 1%, preferably from about 0.1% to about 0.2% by weight. For injection molding applications, high injection molded properties were found for 1.5% silicate content: tensile strength of 91 MPa, modulus of 3.4 GPa and ultimate elongation of 47%, whereas a typical neat nylon 6,6 homopolymer would display 80 MPa, 3.0 GPa, and 60%, respectively.

Fiber applications

Fiber applications via the in-situ polymerization approach benefit from the lower modulus targets vs. plastic molding applications, such that lower clay concentration levels may be used where nanoscale interactions play a greater role. Higher orientation levels can be generated in the fiber spinning and drawing processes than in injection molding. The use of higher draw temperature further improves nanocomposite yarn performance by controlling molecular deformation. Luster, smoothness (absence of nubs) and opacity are indicators of the residual particle size of the clay inclusions in spun and drawn fibers.

Solid State Polymerization of in-situ polymerized nanocomposites

Solid state polymerization was performed for 1.5 hours at 200°C using nylon 6,6 which had been in-situ polymerized with four different silicates. Molecular weights were determined before and after solid state polymerization. The nanocomposite samples were found to increase in molecular weight similarly to neat nylon 6,6.

Clay Type	% silicate	Initial MW	Final MW
montmorillonite	1.07	22,500	29,600
laponite RDS	1.93	20,700	28,700
sepiolite	0.98	20,100	25,500
sepiolite	1.73	21,500	28,300

-68-

Comparison of compositions from in-situ polymerization vs. melt compounding.

A well hydrated, never-dried slurry of Mineral Colloid BP (Na-montmorillonite) was added to a 50% nylon 6,6 salt solution, homogenized and polymerized to produce a nanocomposites of 1.0% and 1.25% silicate by weight. The nanocomposites were injection molded and tensile tested according to ASTM method D-638. Comparative nanocomposites were compounded on a twin screw extruder from similar montmorillonites that were pre-treated with ammonium compounds to allow their intercalation and exfoliation by a nylon melt, as taught in our earlier patent application. The two treatments, which produced nearly identical results, were dimethyldihydrogenated tallow ammonium and dimethyl(ethylhexyl)hydrogenated tallow ammonium cations. Tensile modulus data plotted as a function of the mineral content of the nanocomposite show the in-situ polymerized compositions to have higher performance at the same loading as the comparative materials made by melt compounding (Figure). Both are superior to traditional composites filled with kaolin clay that is not exfoliated into nanoparticles.

CLAIMS

1. A process to prepare a polyamide nanocomposite composition, the process comprising:
forming an aqueous mixture of a silicate material and a polyamide monomer; and
treating the mixture to polymerize the polyamide monomer forming a polyamide
nanocomposite composition.
2. The process of claim 1, wherein the polyamide is nylon 6, nylon 6,6, nylon 4,6, nylon 6,9,
nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons, or
copolymers thereof.
3. The process of claim 1, wherein the polyamide is a copolymer of nylon 6,6 and nylon 6.
4. The process of claim 1, wherein the monomer is hexamethylene adipamide, ϵ -caprolactam,
lauryllactam, ϵ -caprolactone, or lauryllactone.
5. The process of claim 1, wherein the monomer is hexamethylene adipamide.
6. The process of claim 1, wherein the monomer is a mixture of hexamethylene adipamide and
 ϵ -caprolactam.
7. The process of claim 1, wherein the silicate material is laponite, hectorite, sepiolite, saponite,
attapulgite, or montmorillonite.
8. The process of claim 1, wherein the silicate material is added in fully hydrated form, in the
form of a never-dried slurry, in the form of an aqueous slurry, or in the form of an aqueous
suspension.
9. The process of claim 1, wherein the silicate material is a colloidal dispersion of fully
hydrated exfoliated silicate material in water.
10. The process of claim 1, wherein the silicate material is an organically treated silicate.
11. The process of claim 1, wherein the mixture further comprises a dispersing agent.
12. The process of claim 11, wherein the dispersing agent is a sodium polymethacrylate.
13. The process of claim 1, wherein the mixture further comprises a silane.
14. The process of claim 13, wherein the silane is aminopropyltriethoxysilane.
15. The process of claim 1, wherein the concentration of silicate material in the polyamide
nanocomposite composition is less than about 2 weight percent.

-70-

16. The process of claim 1, wherein the concentration of silicate material in the polyamide nanocomposite composition is less than about 1 weight percent.
17. The process of claim 1, wherein the concentration of silicate material in the polyamide nanocomposite composition is between about 0.05 weight percent and about 0.2 weight percent.
18. The process of claim 1, wherein the mixture has a higher molar concentration of hexamethylene diamine than adipic acid.
19. The process of claim 1, wherein the mixture further comprises an oligomer of the polyamide monomer or a low molecular weight polymer of the polyamide monomer prior to the polymerization step.
20. The process of claim 1, further comprising dissociating at least about 50% of the silicate material.
21. The process of claim 20, wherein the silicate material is dissociated by a mechanical unit, pressure alteration, ultrasonics, a stirrer, or a high shear homogenizer.
22. A polyamide nanocomposite composition prepared by the method of claim 1.
23. A polyamide nanocomposite composition comprising a polyamide and a silicate material, wherein the tensile modulus of the composition is higher than the tensile modulus of a composition comprising the identical concentration of components prepared by melt intercalation.

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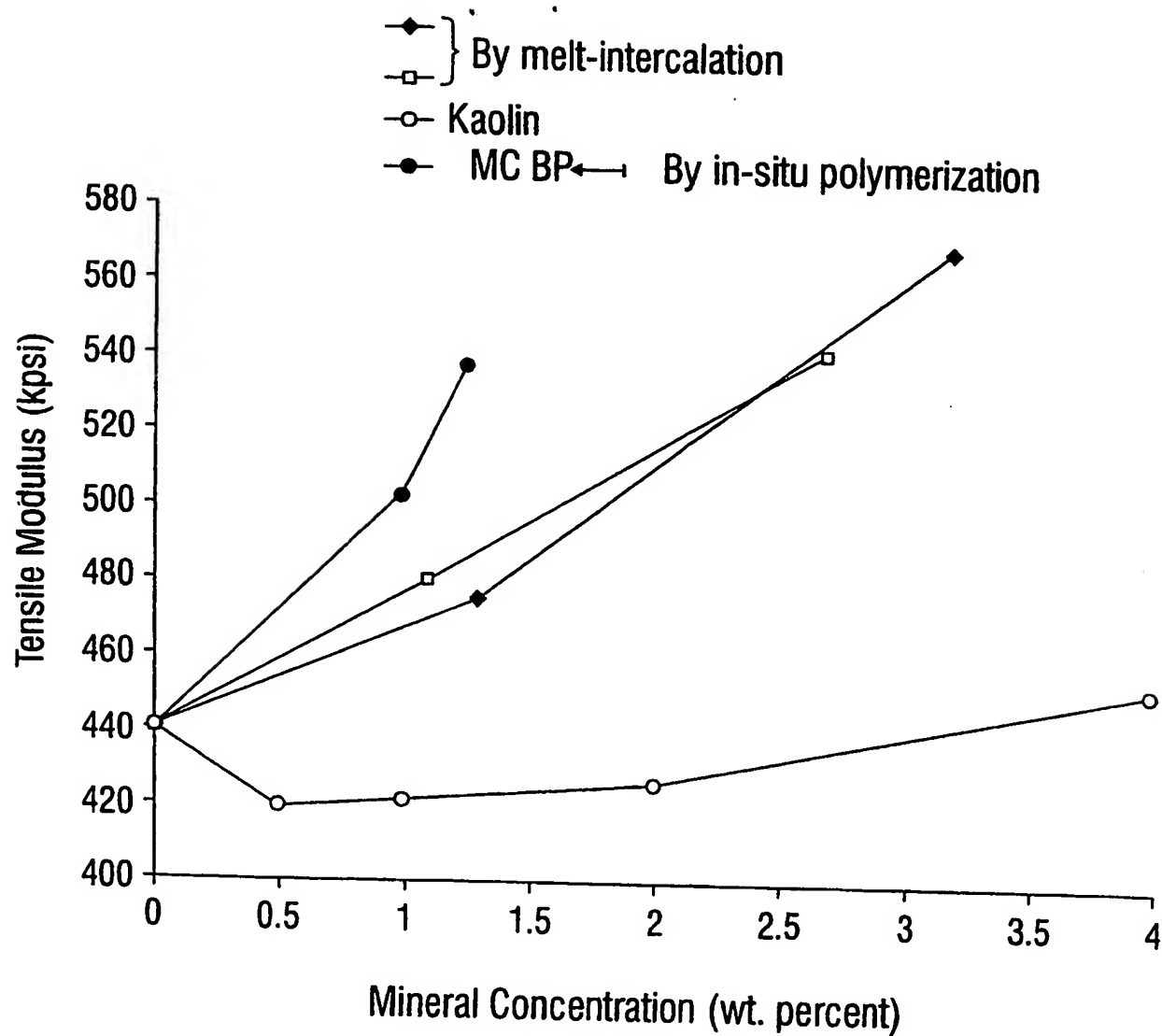


FIG. 1

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F2/44 C08G85/00 C08K3/34 C08K9/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C08G C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 398 551 A (UBE INDUSTRIES ; TOYOTA MOTOR CO LTD (JP); TOYODA CHUO KENKYUSHO KK) 22 November 1990 (1990-11-22) example 1	1-23
X	US 4 810 734 A (KAWASUMI MASAYA ET AL) 7 March 1989 (1989-03-07) example 1 claim 1	1-23
X	US 4 739 007 A (OKADA AKANE ET AL) 19 April 1988 (1988-04-19) example 1 claims 1,8	1-23

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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